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Pyran-fused non-fullerene acceptor achieving 15.51% efficiency in organic solar cells

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ABSTRACT

Despite the rapidly increasing power conversion efficiency (PCE) of organic solar cells (OSCs), the involved lightharvesting materials in excellent devices still suffer from tedious and inefficient synthesis. This creates one rather challenging issue for both further optimization in lab and large-scale production of OSCs. Herein, based on a pyran-fused backbone, an accessible and largely promising feasible non-fullerene acceptor (NFA) **FOEH-2F** has been designed and efficiently synthesized, which displays a much stronger near-infrared absorption and more compact molecular packing with respect to that of its control molecule **F-EH-2F**. As a result, OSC based on **FOEH-2F** affords a considerable PCE of 15.51%, the highest performance reported to date for pyran-fused NFAs.

1. Introduction

As one of the sustainable solar energy-harvesting technologies, organic solar cells (OSCs) have drawn considerable attentions owing to its great potential for solution-processed large-area production, flexible and wearable devices, and semi-transparent/indoor photovoltaic applications [1-7]. In the past decades, tremendous progress of OSCs should be mainly attributed to the invention of novel light-harvesting materials. Among them, the recently developed non-fullerene acceptors (NFAs) with an acceptor-donor-acceptor (A-D-A) architecture have attracted extensive attentions due to their distinctive advantages of superior charge separation and transport features originating from their unique frontier electron density distributions [8–11]. Especially in 2019, a Y-series acceptor, e.g., Y6, emerged as a new-generation NFAs, and following this, further chemical modifications on its central units [12–17], spacers [18–20], side chains [21–25] and end groups [26–33] have boosted the PCEs of state-of-the-art OSCs towards 20% [34-36]. However, when taking the absorption of the applied Y-series NFAs into consideration, there are still much room for extending the absorption onset to approach the theoretical PCE of OSCs. Furthermore, in terms of the synthesis of Y-series molecules, several vital challenges including the complicated structures of building block, rigorous reaction conditions and low yields have made the best Y-series rather challenging for scalable production at the current stage [37–41]. Fortunately, in view of the vast diversity of chemical structures of organic materials, there is no doubt that more molecules affording performances similar or even better than those of Y-series NFAs might be designed and efficiently synthesized through more straightforward synthetic routes. Hence, further innovative exploration for light-harvesting materials combining both efficient synthesis and high PCEs, is not only indispensable for large-scale production of OSCs but also highly important in view of the property-structure relationship understanding.

Fluorene as a planar and rigid skeleton is widely available and has been firstly applied into the fused ring NFAs by our group to construct **FDICTF** molecule [42]. Note that the central donor part of **FDICT** can be efficiently synthesized and easily scaled up to 10 g in laboratory. Later, by combining fluorene based central donors with different electron-withdrawing terminals, a series of NFAs, e.g., **F–2F**, **F–Br** and **FDNCTF**, have been developed [43–45]. A systematical investigation of OSCs based on above F-series NFAs demonstrates rather favorable

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characteristics of both high open-voltage (V_{oc}) and fill factors (FF), leading to very encouraging PCEs of 13.8% and 17.3% for single junction and tandem devices, respectively [46,47]. However, during the efforts to further improve the PCEs of F-series NFAs based devices, we found that the relatively small short current density (J_{sc}) caused by their insufficient light-absorption is the major limitation to further enhance their performance [1,48–50]. Importantly, based on our semi-empirical model for efficient OSCs, over 20% PCEs can be achieved immediately if the range of absorption onset is extended to 950–1100 nm for a single junction OSC on the basis of average external quantum efficiency (EQE) of 80%, energy loss (E_{loss}) of below 0.45 eV and FF of 80% [43,47]. Therefore, further enhancing the near-infrared (NIR) absorption of structurally simple F-series NFAs by chemical modification has been regarded as one important approach to achieve state-of-the-art OSCs and beyond for potential commercial application in the near future.

With these in mind, two A-D-A-type NFAs, denoted as F-EH-2F and FOEH-2F (Scheme 1a), were designed and synthesized. It is worth noting that both acceptors can be easily available in a few steps with high yields from commercial raw materials, demonstrating their great potential to meet the easily synthesis requirement for large-scale production. Furthermore, in view of the light-harvesting ability, the onset absorption of FOEH-2F based on a pyran-fused backbone redshifts significantly towards NIR region with respect to that of F-EH-2F or other F-series NFAs mentioned above. As expected, when blending FOEH-2F with a well-known PM6 donor as the active layer of OSCs [51], a good PCE of 14.53% can be achieved with a markedly increased J_{sc} of 22.81 mA cm⁻² comparing to that (17.71 mA cm⁻²) of OSC based on **F-EH-2F**. More importantly, when blended with another preferable donor D18 [52-55], FOEH-2F affords a considerably higher PCE of 15.51%, along with the overall upgraded $V_{\rm oc}$ of 0.880 V, $J_{\rm sc}$ of 23.75 mA cm⁻² and FF of 74.2%. Note that D18:FOEH-2F system is one of the most efficient material systems for high performance OSCs beyond Y6 systems, in addition to its advantages in terms of simple and efficient synthesis.

2. Results and discussion

2.1. Synthesis and thermal stability

The synthetic routes to F-EH-2F and FOEH-2F were depicted in

Scheme 1b, which are similar to that in our previous reports [42,43,56]. Quite different from Y-series NFAs, both molecules could be obtained with over 85% yields in each step from commercially available raw materials. The involved reactions are all classical reactions with relatively mild conditions, in favor of large-scale production and commercialization. The detailed synthesis procedures were described in Scheme S1 (Supporting Information) and the chemical structures of all the intermediates and targeted NFAs have been fully characterized and confirmed by their ¹H NMR, ¹³C NMR and HRMS analysis (Fig. S7~20). Both NFAs exhibit a good solubility over 10 mg/mL in common organic solvents, such as chloroform, chlorobenzene and toluene, which will be beneficial for the solution-processing device fabrication. In addition, based on the acquired thermogravimetric analysis (TGA) curves shown in Fig. S1, both NFAs of F-EH-2F and FOEH-2F possess good thermal stability with high decomposition temperatures (T_d) of 317 and 322 °C, respectively.

2.2. Light absorption and energy levels

The normalized ultraviolet-visible (UV-vis) absorption spectra of NFAs in both chloroform solutions and thin films were shown in Fig. 1a, and the detailed parameters were summarized in Table 1. As it can be expected, FOEH-2F displays the maximum absorption peak (λ_{max}^{sol}) of 705 nm in chloroform solution, red-shifting by 34 nm comparing to that of 671 nm for F-EH-2F, demonstrating that the electron-rich oxygen insertion into the backbone could work as an effective strategy to construct NIR NFAs. From solutions to solid films, much red-shifted absorptions could be observed for both NFAs with maximum absorption peaks (λ_{max}^{film}) at 698 nm for **F-EH-2F** and 781 nm for **FOEH-2F**. Note that a ~76 nm red-shift has been observed for FOEH-2F from solution to solid film, much larger than that of ~27 nm for F-EH-2F, suggesting a stronger intermolecular action for FOEH-2F [57]. As a consequence, **F-EH-2F** and **FOEH-2F** films possess onset absorptions (λ_{onset}^{film}) at 753 and 852 nm, corresponding to an optical bandgap (E_g^{opt}) of 1.65 and 1.46 eV, respectively. Note that FOEH-2F film displays a highly strong absorption in a broad wavelength range of 650-850 nm, which is complementary to those of the state-of-the-art polymeric donors of PM6 and D18 (Fig. 1b), rendering PM6:FOEH-2F or D18:FOEH-2F blends promising for efficient OSCs with relatively large J_{sc} .



Scheme 1. (a) Chemical structures of acceptors F-EH-2F, FOEH-2F and donors PM6, D18; (b) the detailed synthetic routes of two acceptors.



Fig. 1. (a) The normalized absorption spectra of F-EH-2F and FOEH-2F as pristine films and in chloroform solution; (b) blend films; (c) the energy levels of F-EH-2F, FOEH-2F, PM6 and D18 estimated from CV; (d) Inverted device structure of the OSCs; (e) *J*–*V* characteristics; (f) EQE spectra of OSCs based on F-EH-2F and FOEH-2F at optimal conditions.

 Table 1

 Optoelectronic properties of F-EH-2F, FOEH-2F, PM6 and D18.

Comp.	λ_{max}^{sol} $(nm)^a$	λ ^{film} (nm)	λ ^{film} (nm)	E_g^{opt} (eV) ^b	HOMO ^{film} (eV)	<i>LUMO^{film}</i> (eV)	E ^{CV} (eV) ^c
F-EH- 2F	671	698	753	1.65	-5.65	-3.84	1.81
FOEH- 2F	705	781	852	1.46	-5.61	-3.91	1.70
PM6 D18	616 584	624 581	684 625	1.81 1.98	-5.48 -5.51	$-3.66 \\ -2.77$	1.82 2.74

^a The λ_{max}^{sol} obtained from the dilute solution in CF.

 $^{\rm b}$ The optical bandgap estimated from the absorption onset. $E_g^{opt}=1240/\frac{2}{3}$

^c The energy gap derived from cyclic voltammetry measurement.

The electrochemical behaviors of **FOEH-2F** and **F-EH-2F** have also been investigated by cyclic voltammetry (CV) in Fig. S2. The derived energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are presented in Fig. 1c and Table 1. The HOMO and LUMO energy levels of **F-EH-2F** locate at -5.65 and -3.84 eV, respectively. Note that an upshifted HOMO of -5.61 eV and downshifted LUMO of -3.91 eV can be afforded by **FOEH-2F**, giving rise to a much narrower bandgap of 1.70 eV in comparison to that of 1.81 eV for **F-EH-2F**. The largely decreased bandgap of **FOEH-2F** derived from CV is caused by the markedly electron-rich backbone after oxygen insertion and also in good accordance with the optical bandgap obtained from their film absorptions. It is worth mentioning that the energy levels of both **FOEH-2F** and **F-EH-2F** could well match with those of state-of-the-art polymer donors **PM6** and **D18**, affording the sufficient driving forces for exciton dissociation. The alignment of energy levels derived from CVs also agrees well with the calculated ones by employing density functional theory (DFT) at the B3LYP/6-31G* level (Fig. S3). In addition, planar geometries can be maintained by both **FOEH-2F** and **F-EH-2F**, mainly due to their rigid donor backbones and also S–O secondary interaction with electron-withdrawing terminals. The preferable planar backbone will be in favor of the ordered and compact molecular packing, and thus improved charge transport properties [43–45].

2.3. Photovoltaic properties

In order to evaluate the photovoltaic properties of **F-EH-2F** and **FOEH-2F**, OSCs with an inverted architecture of indium tin oxide (ITO)/ ZnO/PFN-Br/Active layers/MoO₃/Ag were fabricated (Fig. 1d). The selected polymeric donors are **PM6** and **D18** because of their suitable energy levels and complementary absorptions. The detailed photovoltaic parameters for champion OSCs based on **F-EH-2F** and **FOEH-2F** are depicted in Table 2, and the corresponding *J-V* characteristics are shown in Fig. 1e.

As shown in Table 2, when blended with PM6, the optimized OSC

Table 2

Parameters of the optimized devices based on F-EH-2F and FOEH-2F.

	-				
Active layers	$V_{\rm oc}$ (V)	J _{sc} (mA cm ⁻²)	J _{cal} (mA cm ⁻²) ^a	FF (%)	PCE (%) ^b
PM6:F- EH-2F	0.963 (0.968 ± 0.003)	17.71 (17.20 ± 0.22)	17.62	70.8 (70.5 ± 0.5)	$\begin{array}{c} 12.08 \\ (11.73 \pm \\ 0.15) \end{array}$
PM6: FOEH- 2F	0.869 (0.863 ± 0.004)	$\begin{array}{c} 22.81 \\ (22.59 \pm \\ 0.29) \end{array}$	22.13	73.3 (73.3 ± 0.8)	14.53 (14.28 \pm 0.17)
D18: FOEH- 2F	0.880 (0.879 ± 0.004)	$\begin{array}{c} 23.75 \\ (23.62 \pm \\ 0.34) \end{array}$	23.08	74.2 (73.8 ± 0.9)	15.51 (15.28 ± 0.14)

^a J_{cal} integrated from the EQE spectrum.

^b The average values from 10 devices.

based on **PM6:F-EH-2F** blend affords a PCE of 12.08% with a large V_{oc} of 0.963 V, J_{sc} of 17.71 mA cm⁻² and FF of 70.8%. It is worth noting that a significantly improved PCE of 14.53% can be achieved by PM6:FOEH-**2F** based OSC, along with a greatly enlarged J_{sc} of 22.81 mA cm⁻², good $V_{\rm oc}$ of 0.869 V and notable FF of 73.3%. Apparently, comparing to that of F-EH-2F, the markedly improved J_{sc} of FOEH-2F based device mainly originates from its significantly enhanced film absorption in NIR region (Fig. 1b) and larger EQE values discussed below. Whereas the much higher V_{oc} of **F-EH-2F** based device should be ascribed to the high-lying LUMO energy levels of F-EH-2F comparing to that of FOEH-2F (Fig. 1c). In view of the already obtained encouraging results for PM6:FOEH-2F based OSCs, we further blended FOEH-2F with a well-known polymeric donor D18, which possesses a downshifted HOMO (thus a higher theorical $V_{\rm oc}$) and higher crystallinity with respect to that of **PM6** [51,52]. As a result, a considerably higher PCE of 15.51% was achieved by D18: FOEH-2F based OSC with an overall upgraded V_{oc} of 0.880 V, J_{sc} of



Fig. 2. (a) $J_{\rm ph}$ vs $V_{\rm eff}$ curves of the optimized devices; (b) The PL spectra of pure NFAs films and blend films; (c) $V_{\rm oc}$ versus light intensity; (d) $J_{\rm sc}$ versus light intensity; (e) TPC curves; (f) TPV curves.

23.75 mA cm⁻² and higher FF of 74.2% comparing to that of **PM6**: **FOEH-2F** based device. Combining this considerable PCEs and easy synthesis features discussed above, **FOEH-2F** has been proven to be among the best NFAs beyond Y-series.

The improved performance of OSCs based on FOEH-2F, relative to that of F-EH-2F, should be mainly attributed to the markedly enlarged J_{sc} , which is in good accordance with the EQE spectra recorded in Fig. 1f. Note that FOEH-2F based devices display a much broader photoelectron response up to 852 nm with the maximum EQE values of ~87% for PM6:FOEH-2F and ~92% for D18:FOEH-2F, much better than that of PM6:F-EH-2F based OSCs with the photo-electron response limiting to 753 nm and the maximum EQE values of \sim 82%. Therefore, the much larger integrated J_{sc} of 22.13 and 23.08 mA cm⁻² could be afforded by PM6:FOEH-2F and D18:FOEH-2F based devices, respectively, comparing to that of 17.62 mA cm^{-2} for **PM6:F-EH-2F** based one. The broader EQE range of FOEH-2F based OSCs should be attributed to their enhanced NIR film absorptions, whereas the superior maximum EQE values should be ascribed to the more favorable film morphologies discussed below. Note that all the integrated J_{sc} values are in good agreement with that from J-V measurements, and the deviations are within 5%.

2.4. Charge dynamics

To further clarify the differences in EQEs and FFs of the three blends based OSCs, the exciton dissociation properties were first investigated by measuring the relationship of the photocurrent density ($J_{\rm ph}$) and effective voltage ($V_{\rm eff}$). The exciton dissociation probability $P_{\rm diss}$ (E, T) could be indicated by the ratio of $J_{\rm ph}$ to $J_{\rm sat}$ where $J_{\rm sat}$ is the saturated $J_{\rm ph}$ at a sufficiently high $V_{\rm eff}$, and all the photogenerated excitons could be dissociated into free carriers and completely collected by the electrodes [58]. As shown in Fig. 2a, the values of $P_{\rm diss}$ (E, T) for **PM6**: **F-EH-2F**, **PM6:FOEH-2F** and **D18:FOEH-2F** based OSCs are 93.7%, 95.3% and 95.5%, respectively, indicating an efficient and also improved exciton dissociation for **FOEH-2F** based device with respect to that of **F-EH-2F** based one. This can be further verified by the slightly more intensive photoluminescence quenching of 97.6% and 97.3% for **PM6:FOEH-2F** and **D18:FOEH-2F** blended films in comparison with that of 96.6% for **PM6:F-EH-2F** blend as displayed in Fig. 2b.

In addition, the light intensity (P_{light} , which varies from 10 to 100 mW cm⁻²) dependence of $J_{\rm sc}$ and $V_{\rm oc}$ were also measured in order to investigate the charge recombination kinetics in OSCs, and the corresponding characteristics have been plotted in Fig. 2c and d. Among them, the relationship between J_{sc} and P_{light} should follows the equation: $J_{\rm sc} \propto P^{\alpha}$, where α is defined as an exponential factor and could indicate the weak bimolecular recombination if the α value is close to unity [59]. As illustrated in Fig. 2d, the α values of the three devices based on **PM6**: F-EH-2F, PM6:FOEH-2F and D18:FOEH-2F are estimated to be 0.971, 0.973 and 0.970, respectively, indicating that the bimolecular recombination is significantly suppressed in these systems. Additionally, the slope (nkT/q) of V_{oc} versus the natural logarithm of P_{light} is usually regarded as the indicator to reflect the charge recombination properties in OSCs under open-circuit condition [60]. As depicted in Fig. 2c, D18: FOEH-2F, PM6:FOEH-2F and PM6:F-EH-2F based devices exhibit the slopes of 1.23, 1.35, and 1.41kT/q, respectively. The smaller slopes of FOEH-2F based devices suggest lower amount of trap-assisted recombination losses especially for that of D18:FOEH-2F, which should account for the slightly larger J_{sc} and FF with respect to that of **PM6**: FOEH-2F based device.

Transient photocurrent (TPC) and transient photovoltage (TPV) measurements were also applied to monitor the charge extraction behaviors and charge carrier lifetimes, respectively. For TPC measurements, a shorter charge extraction time indicates that the free charge carriers can transport faster in the active layer once they are generated at the D/A interface [61]. As it can be observed from Fig. 2e, the charge extraction times of **PM6:F-EH-2F**, **PM6:FOEH-2F** and **D18:FOEH-2F**

based devices are 0.55, 0.51 and 0.45 µs, respectively, indicating that all of them have efficient charge transport but slightly better for D18: FOEH-2F. For TPV tests, a rapid voltage decay usually suggests a large charge recombination in OSCs [62]. As shown in Fig. 2f, the lifetime of charge carriers in F-EH-2F based device is calculated to be 36 µs, whereas the much prolonged lifetimes of 50 and 110 µs can be observed by PM6:FOEH-2F and D18:FOEH-2F based devices, respectively. This indicates that the carrier recombination is greatly inhibited in FOEH-2F based devices especially for that of D18:FOEH-2F, which is in agreement with the suppressed trap-assisted recombination observed in Fig. 2c. Moreover, charge transport properties of the blended films were further investigated by the method of space-charge-limited-current (SCLC). The detailed plots and parameters are shown in Fig. S4 and Table S1. In general, PM6:FOEH-2F and D18:FOEH-2F photoactive lavers exhibit overall ungraded hole/electron mobility (μ_e/μ_h) of 2.57 \times $10^{-4}/1.87 \times 10^{-4}$ and $2.81 \times 10^{-4}/2.23 \times 10^{-4}$ cm² V⁻¹ s⁻¹, respectively, better than that of **PM6:F-EH-2F** based blends $(1.46 \times 10^{-4}/0.99)$ \times 10⁻⁴ cm² V⁻¹ s⁻¹). The both enlarged hole and electron mobility of **FOEH-2F** based devices should contribute to their improved J_{sc} and FF. Note that the D18:FOEH-2F blended films afford a hole/electron mobility ratio of 1.26, more balanced than that of 1.37 for PM6: FOEH-2F blended films, which should be responsible for the simultaneously enhanced J_{sc} and FF of D18:FOEH-2F based OSCs [63].

To sum up, **FOEH-2F** based devices possess slightly improved exciton dissociation efficiencies, better charge carrier transport properties and lower degree of charge recombination with respect to that of **F-EH-2F** based devices. All the favorable factors mentioned above in combination support the high J_{sc} and FF values of **FOEH-2F** based devices. We also found that a suppressed charge recombination and more balanced hole/ electron mobility can be achieved after varying the polymeric donor from **PM6** to **D18** originating from **D18**'s higher crystallinity. This should account for the further improved J_{sc} and FF for **D18:FOEH-2F** based OSC with respect to that of **PM6:FOEH-2F** based ones.

2.5. Morphology analysis

The microscopic morphology of the active layer usually plays a dominant role in the exciton dissociation, charge transport and recombination dynamics and thus their photovoltaic performance OSCs [64]. Therefore, atomic force microscopy (AFM) and transmission electron microscopy (TEM) technologies were firstly employed to unveil the morphology change of these active layers at a level of nanoscale. As observed from the AFM images in Fig. 3a~c, the root-mean-square (RMS) roughness values of PM6:F-EH-2F, PM6:FOEH-2F and D18: FOEH-2F blend films can be determined as 1.53, 1.08 and 1.09 nm, respectively. Note that both FOEH-2F based systems exhibit more uniform and smooth upper surface topographies than that of F-EH-2F based one, which could ensure the intimate contacts with the charge transport layers and thus the efficient charge transfer at the interface. For a preferred blend morphology, bi-continuous interpenetrating networks and nanoscale phase separations are required. Fig. 3d~f displayed the TEM images of these three blended films, demonstrating clear fiber structures and nanoscale phase separation in FOEH-2F based blends especially for that of D18:FOEH-2F. In sharp contrast to that of PM6: F-EH-2F blend, the fiber structures of FOEH-2F based blends should result from its stronger molecular aggregation behavior discussed below. Note that compared with PM6:FOEH-2F, more clear fibers could be observed by D18:FOEH-2F blend, which is possibly due to the much higher crystallinity of D18 with respect to that of PM6 [52]. Originating from the above favourable morphology, Jsc and FF of the FOEH-2F based devices are improved simultaneously from PM6 to D18.

In order to further provide a deeper insight into the effects of oxygeninserted backbone of **FOEH-2F** on its molecular packing, the grazingincidence wide-angle X-ray scattering (GIWAXS) was performed. The resulting 2D GIWAXS patterns and 1D profiles of both pristine NFAs and blends have been depicted inFig. 4af and Fig. S5a5d. As shown in Fig. 4a,



Fig. 3. (a), (b), (c) AFM height images; (d), (e), (f) TEM images of PM6:F-EH-2F, PM6:FOEH-2F and D18:FOEH-2F optimized films.



Fig. 4. 2D GIWAXS image of pristine NFAs (a) F-EH-2F, (b) FOEH-2F and blend films (d) PM6:FOEH-2F, (e) D18:FOEH-2F after 130 °C TA 10 min; 1D plots extracted from the 2D patterns along the OOP and IP directions of the corresponding pristine NFAs (c) and blend films (f).

b and Table 3, FOEH-2F neat film exhibits a more preferential face-on orientation than F-EH-2F, indicated by the stronger (010) diffraction peak in the out-of-plane (OOP) direction [43,47]. Moreover, quite different from that of F-EH-2F, numerous obvious diffraction rings located at a range of 0.5–2 Å⁻¹ in both in-plane (IP) and OOP directions have been observed for FOEH-2F neat film, indicating that FOEH-2F is highly crystallized [65]. Among them, the diffraction rings locating at q_z of 0.53, 1.26 and 1.48 Å⁻¹ are preferentially stronger in the OOP direction, which should be indexed as the (001), (002) and (003) diffraction peaks of flat-on lamellar crystalline of FOEH-2F backbone, while the diffraction peak at q_z = 1.86 Å⁻¹ is attributed to the (010) π - π

stacking within FOEH-2F crystals [65]. Besides, both F-EH-2F and FOEH-2F exhibit strong (010) peaks in the out-of-plane direction, locating at 1.81 and 1.86 Å⁻¹ for F-EH-2F and FOEH-2F and corresponding to the π - π stacking distance (d_{010}) of 3.46 and 3.38 Å, respectively. As a result, the molecular packing is getting more compact from F-EH-2F to FOEH-2F, thus leading to a larger red-shifted absorption, improved charge transport and suppressed charge carrier recombination discussed above. In addition, as shown in Fig. S6b~6d, the same phenomenon could be also observed by the two polymeric donors of PM6 and D18, unveiling that D18 possesses a stronger crystallinity in comparison with that of PM6, which is in good accordance with the

Table 3

Summary of th	e GIWAXS	parameters	for	blend	films.
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Active layers	Q (010, Å ⁻¹) ^a	D (010, Å) ^b	FWHM (010, Å ⁻¹) ^c	CCL (010, Å) ^d	Q (100, Å ⁻¹)	D (100, Å)
F-EH-2F	1.81	3.46	0.43	13.04	0.35	18.11
FOEH-2F	1.86	3.38	0.18	31.16	0.35	18.11
PM6:F-	1.82	3.45	0.26	21.81	0.31	20.19
EH-2F						
PM6:	1.79	3.51	0.30	18.71	0.33	19.30
FOEH-						
2F						
D18:	1.80	3.49	0.30	19.08	0.33	18.88
FOEH- 2F						

^a The location of diffraction peaks.

^b The π - π stacking distance.

^c The full width at half maxima of peaks.

 $^d\,$ The crystal coherence lengths calculated from the Scherrer equation: CCL = $2\pi k/FWHM.$

literature report [22,66].

As for the blended films of **PM6:F-EH-2F**, **PM6:FOEH-2F** and **D18**: **FOEH-2F** in Fig. 4d~f, the predominant face-on orientation of NFAs' molecular packing was preserved. As summarized in Table 3, the (010) peaks of **PM6:FOEH-2F** and **D18:FOEH-2F** are located at 1.79 and 1.80 Å⁻¹, corresponding to a π - π stacking distance (d_{010}) of 3.51 and 3.49 Å, respectively. Accordingly, the coherence lengths of the π - π stacking (CCL₀₁₀) for **PM6:FOEH-2F** and **D18:FOEH-2F** blends were obtained based on the Scherrer equation (*CCL* = $2\pi k/FWHM$), being 18.71 and 19.08 Å, respectively. The stronger π - π stacking and slightly enlarged CCL in **D18:FOEH-2F** blend comparing to that of **PM6:FOEH-2F** should be caused by the higher crystallinity of **D18**, resulting in better electron transport properties, more suppressed charge recombination and thus improved J_{sc} and FF of the devices [66].

2.6. Eloss analysis

To disclose the inner relationship of structure-energy loss (E_{loss}), we analysed the E_{loss} s of OSCs based on the detailed balance theory [67]. According to the Shockley-Queisser (SQ) limit, E_{loss} in OSCs contains three parts [27], as shown in the following formula:

$$E_{loss} = (E_g - qV_{oc}^{SQ}) + (qV_{oc}^{sQ} - qV_{oc}^{rad}) + (qV_{oc}^{rad} - qV_{oc})$$

 $= \Delta E_1 + \Delta E_2 + \Delta E_3$

Among them, the energy bandgaps (E_g) of OSCs could be estimated from the intersection of the optical absorption and EL curves of corresponding blend films [67], being 1.704 eV for **PM6:F-EH-2F**, 1.557 eV for both **PM6:FOEH-2F** and 1.548 eV for **D18:FOEH-2F** blends (Fig. S6a, b, c). Thus the total E_{loss} of OSCs can be calculated based on the following equation: $E_{loss} = (E_g - qV_{oc})$, being 0.733, 0.691 and 0.665 eV for **PM6:F-EH-2F**, **PM6:FOEH-2F** and **D18:FOEH-2F**, respectively, demonstrating a great reduction of E_{loss} after adopting oxygen-inserted backbone in **FOEH-2F** acceptor (see Table 4).

In order to get a deeper insight into the origin of energy losses in OSCs studied here, all the three parts of energy losses have been eval-

uated. The detailed calculation method of three parts of energy losses was depicted in Supporting Information. Among them, ΔE_1 is the radiative loss above bandgap and unavoidable in all types of solar cells [67]. The values of ΔE_1 are determined by the energy offset between the bandgap (E_g) of OSCs and the qV_{oc} in the Shockley-Queisser (SQ) limit (qV_{oc}^{SQ}) , which have been calculated as 0.281, 0.272 and 0.272 eV for PM6:F-EH-2F. PM6:FOEH-2F and D18:FOEH-2F based OSCs, respectively. ΔE_2 represents the radiative loss below bandgap and can be evaluated by the energy offset between qV_{oc}^{SQ} and qV_{oc} in the radiative limit (qV_{α}^{rad}). Note that relatively smaller ΔE_2 of 0.126 and 0.115 eV have been achieved by PM6:FOEH-2F and D18:FOEH-2F based OSCs with respect to that of 0.130 eV for **PM6:F-EH-2F** based one. ΔE_3 indicates the non-radiative energy loss and reflects the energy offset between qV_{oc}^{rad} and qV_{oc} existing in real OSCs. The greatly suppressed non-radiative recombination with much reduced ΔE_3 of 0.293 and 0.278 eV has been achieved by PM6:FOEH-2F and D18:FOEH-2F based OSCs, respectively, in sharp comparison to that of 0.322 eV for PM6: **F-EH-2F** (Fig. 5a). Moreover, the reduced ΔE_3 for **FOEH-2F** based OSCs could be further confirmed by their much higher external electroluminescence quantum efficiency (EQE_{EL}) as shown in Fig. 5b. Therefore, the much lower energy losses achieved by FOEH-2F based OSCs should be ascribed to the suppressed recombination especially for the non-radiative recombination.

As proved by recent studies [68–71], non-radiative recombination loss (ΔE_3) and energetic disorder, which are closely related to the tail states below the band edge and the over-all photon energy loss, need to be minimized to improve cell performance [72] In the range of low photon energy, the optical absorption coefficient ($\alpha(E)$) of disordered organic semiconductors follows the Urbach rule as described by the following formula [73].

 $\alpha(E) = \alpha_0 e^{[(E-E_0)/E_U]}$

where the two constants of α_0 represents the optical absorption coefficient at the band edge, E is the photon energy, $E_{\rm U}$ represents the Urbach energy which is usually described as a measure of energetic disorder [29]. Generally, a smaller $E_{\rm U}$ indicates a smaller degree of energy disorder, which should be in favor of the reduction of recombination losses in OSCs [74]. As shown in Fig. 5c, by measuring the high-resolution Fourier transform photocurrent spectroscopy EQE spectra (FTPS-EQE), the much smaller $E_{\rm U}$ of 26.4 and 25.8 meV can be afforded by **PM6**: FOEH-2F and D18:FOEH-2F based devices, respectively, comparing to that of 37.3 meV for PM6:F-EH-2F based one. Note that the slightly reduced E_U of D18:FOEH-2F in comparison with that of PM6:FOEH-2F could be also suggested by its sharper absorption onset (Fig. 1b) and slightly enlarged CCL (Table 3) [38]. The more ordered and compact molecular stacking of both FOEH-2F and D18 should account for the significantly reduced energetic disorder and thus migrate the recombination loss of OSCs [22,74,75].

3. Conclusion

To sum up, two NFAs of **F-EH-2F** and **FOEH-2F** featuring with effective synthesis, were designed and synthesized. Compared with its control molecule of **F-EH-2F**, **FOEH-2F** with a pyran-fused backbone

Table 4

Detailed energy losses of three OSCs based on F-EH-2F and FOEH-2F.

E_{loss} (eV)
0.733
0.691
0.665
b

^a Band gaps estimated via the intersection of normalized absorption and EL spectra.

^b The Exp. results were calculated by following the equation: $qV_{oc}^{non-rad} = -kTln(EQE_{EL})$ [27].



Fig. 5. (a) The E_{loss} distribution of the corresponding devices; (b) EQE_{EL} curves of OSCs at various current densities; (c) The Urbach energy (E_{U}) by measuring the FTPS-EQE.

exhibits a much narrower bandgap and tighter molecular stacking. As a consequence, OSC based on **D18:FOEH-2F** blend affords a considerable PCE of 15.51%, making it not only the highest value reported to date for pyran based NFAs, but also one relatively high efficient system beyond **Y6** system. More importantly, when further taking the effective synthesis of **FOEH-2F** into consideration, this system would offer some advantage for large-scale production of OSCs. Our work will stimulate further innovative explorations for active materials with both high efficiency and simple synthesis, aiming to boost OSCs towards commercial application.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2022.106541.

References

 F. Bai, J. Zhang, A. Zeng, H. Zhao, K. Duan, H. Yu, K. Cheng, G. Chai, Y. Chen, J. Liang, W. Ma, H. Yan, A highly crystalline non-fullerene acceptor enabling efficient indoor organic photovoltaics with high EQE and fill factor, Joule 5 (2021) 1231–1245.

- [2] C.J. Brabec, A. Distler, X. Du, H.J. Egelhaaf, J. Hauch, T. Heumueller, N. Li, Material strategies to accelerate OPV technology toward a GW technology, Advanced Energy Materials 10 (2020), 2001864.
- [3] D. Koo, S. Jung, J. Seo, G. Jeong, Y. Choi, J. Lee, S.M. Lee, Y. Cho, M. Jeong, J. Lee, J. Oh, C. Yang, H. Park, Flexible organic solar cells over 15% efficiency with polyimide-integrated graphene electrodes, Joule 4 (2020) 1021–1034.
- [4] B. Lin, X. Zhou, H. Zhao, J. Yuan, K. Zhou, K. Chen, H. Wu, R. Guo, M.A. Scheel, A. Chumakov, S.V. Roth, Y. Mao, L. Wang, Z. Tang, P. Müller-Buschbaum, W. Ma, Balancing the pre-aggregation and crystallization kinetics enables high efficiency slot-die coated organic solar cells with reduced non-radiative recombination losses, Energy & Environmental Science 13 (2020) 2467–2479.
- [5] W. Song, B. Fanady, R. Peng, L. Hong, L. Wu, W. Zhang, T. Yan, T. Wu, S. Chen, Z. Ge, Foldable semitransparent organic solar cells for photovoltaic and photosynthesis, Advanced Energy Materials 10 (2020), 2000136.
- [6] R. Sun, Q. Wu, J. Guo, T. Wang, Y. Wu, B. Qiu, Z. Luo, W. Yang, Z. Hu, J. Guo, M. Shi, C. Yang, F. Huang, Y. Li, J. Min, A layer-by-layer architecture for printable organic solar cells overcoming the scaling lag of module efficiency, Joule 4 (2020) 407–419.
- [7] D. Wang, H. Liu, Y. Li, G. Zhou, L. Zhan, H. Zhu, X. Lu, H. Chen, C.-Z. Li, Highperformance and eco-friendly semitransparent organic solar cells for greenhouse applications, Joule 5 (2021) 945–957.
- [8] X. Wan, C. Li, M. Zhang, Y. Chen, Acceptor-donor-acceptor type molecules for high performance organic photovoltaics - chemistry and mechanism, Chem Soc Rev 49 (2020) 2828–2842.
- [9] J. Wang, X. Zhan, Fused-ring electron acceptors for photovoltaics and beyond, Acc Chem Res 54 (2021) 132–143.
- [10] Y. Lin, J. Wang, Z.G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, An electron acceptor challenging fullerenes for efficient polymer solar cells, Adv Mater 27 (2015) 1170–1174.
- [11] C. Yan, S. Barlow, Z. Wang, H. Yan, A.K.Y. Jen, S.R. Marder, X. Zhan, Non-fullerene acceptors for organic solar cells, Nature Reviews Materials 3 (2018) 18003.
- [12] C. Zhu, K. An, W. Zhong, Z. Li, Y. Qian, X. Su, L. Ying, Design and synthesis of nonfullerene acceptors based on a quinoxalineimide moiety as the central building block for organic solar cells, Chem Commun (Camb) 56 (2020) 4700–4703.
- [13] C. Zhang, J. Yuan, K.L. Chiu, H. Yin, W. Liu, G. Zheng, J.K.W. Ho, S. Huang, G. Yu, F. Gao, Y. Zou, S.K. So, A disorder-free conformation boosts phonon and charge transfer in an electron-deficient-core-based non-fullerene acceptor, Journal of Materials Chemistry A 8 (2020) 8566–8574.
- [14] W. Liu, J. Zhang, S. Xu, X. Zhu, Efficient organic solar cells achieved at a low energy loss, Science Bulletin 64 (2019) 1144–1147.
- [15] F. Lin, K. Jiang, W. Kaminsky, Z. Zhu, A.K. Jen, A non-fullerene acceptor with enhanced intermolecular pi-core interaction for high-performance organic solar cells, J Am Chem Soc 142 (2020) 15246–15251.
- [16] R. Wang, J. Yuan, R. Wang, G. Han, T. Huang, W. Huang, J. Xue, H.C. Wang, C. Zhang, C. Zhu, P. Cheng, D. Meng, Y. Yi, K.H. Wei, Y. Zou, Y. Yang, Rational tuning of molecular interaction and energy level alignment enables highperformance organic photovoltaics, Adv Mater 31 (2019), e1904215.

M. Li et al.

- [17] Z. Zhou, W. Liu, G. Zhou, M. Zhang, D. Qian, J. Zhang, S. Chen, S. Xu, C. Yang, F. Gao, H. Zhu, F. Liu, X. Zhu, Subtle molecular tailoring induces significant morphology optimization enabling over 16% efficiency organic solar cells with efficient charge generation, Adv Mater 32 (2020), e1906324.
- [18] K. Jiang, Q. Wei, J.Y.L. Lai, Z. Peng, H.K. Kim, J. Yuan, L. Ye, H. Ade, Y. Zou, H. Yan, Alkyl chain tuning of small molecule acceptors for efficient organic solar cells, Joule 3 (2019) 3020–3033.
- [19] L. Hong, H. Yao, Z. Wu, Y. Cui, T. Zhang, Y. Xu, R. Yu, Q. Liao, B. Gao, K. Xian, H. Y. Woo, Z. Ge, J. Hou, Eco-compatible solvent-processed organic photovoltaic cells with over 16% efficiency, Adv Mater 31 (2019), e1903441.
- [20] S. Dong, T. Jia, K. Zhang, J. Jing, F. Huang, Single-component non-halogen solvent-processed high-performance organic solar cell module with efficiency over 14, Joule 4 (2020) 2004–2016.
- [21] S. Bao, H. Yang, H. Fan, J. Zhang, Z. Wei, C. Cui, Y. Li, Volatilizable solid additiveassisted treatment enables organic solar cells with efficiency over 18.8% and fill factor exceeding 80, Adv Mater 33 (2021), e2105301.
- [22] Y. Chen, F. Bai, Z. Peng, L. Zhu, J. Zhang, X. Zou, Y. Qin, H.K. Kim, J. Yuan, L. K. Ma, J. Zhang, H. Yu, P.C.Y. Chow, F. Huang, Y. Zou, H. Ade, F. Liu, H. Yan, Asymmetric alkoxy and alkyl substitution on nonfullerene acceptors enabling high-performance organic solar cells, Advanced Energy Materials 11 (2020), 2003141.
- [23] A.M.H. Cheung, H. Yu, S. Luo, Z. Wang, Z. Qi, W. Zhou, L. Arunagiri, Y. Chang, H. Yao, H. Ade, H. Yan, Incorporation of alkylthio side chains on benzothiadiazolebased non-fullerene acceptors enables high-performance organic solar cells with over 16% efficiency, Journal of Materials Chemistry A 8 (2020) 23239–23247.
- [24] C. Li, J. Zhou, J. Song, J. Xu, H. Zhang, X. Zhang, J. Guo, L. Zhu, D. Wei, G. Han, J. Min, Y. Zhang, Z. Xie, Y. Yi, H. Yan, F. Gao, F. Liu, Y. Sun, Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells, Nature Energy 6 (2021) 605–613.
- [25] J. Zhang, F. Bai, I. Angunawela, X. Xu, S. Luo, C. Li, G. Chai, H. Yu, Y. Chen, H. Hu, Z. Ma, H. Ade, H. Yan, Alkyl-Chain branching of non-fullerene acceptors flanking conjugated side groups toward highly efficient organic solar cells, Advanced Energy Materials (2021), 2102596.
- [26] Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao, J. Hou, Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages, Nat Commun 10 (2019) 2515.
- [27] S. Li, L. Zhan, N. Yao, X. Xia, Z. Chen, W. Yang, C. He, L. Zuo, M. Shi, H. Zhu, X. Lu, F. Zhang, H. Chen, Unveiling structure-performance relationships from multi-scales in non-fullerene organic photovoltaics, Nat Commun 12 (2021) 4627.
- [28] X. Li, M.-A. Pan, T.-K. Lau, W. Liu, K. Li, N. Yao, F. Shen, S. Huo, F. Zhang, Y. Wu, X. Li, X. Lu, H. Yan, C. Zhan, Roles of acceptor guests in tuning the organic solar cell property based on an efficient binary material system with a nearly zero hole-transfer driving force, Chemistry of Materials 32 (2020) 5182–5191.
- [29] Y. Pan, X. Zheng, J. Guo, Z. Chen, S. Li, C. He, S. Ye, X. Xia, S. Wang, X. Lu, H. Zhu, J. Min, L. Zuo, M. Shi, H. Chen, A new end group on nonfullerene acceptors endows efficient organic solar cells with low energy losses, Advanced Functional Materials (2021), 2108614.
- [30] R. Qin, D. Wang, G. Zhou, Z.-P. Yu, S. Li, Y. Li, Z.-X. Liu, H. Zhu, M. Shi, X. Lu, C.-Z. Li, H. Chen, Tuning terminal aromatics of electron acceptors to achieve highefficiency organic solar cells, Journal of Materials Chemistry A 7 (2019) 27632–27639.
- [31] C. Sun, S. Qin, R. Wang, S. Chen, F. Pan, B. Qiu, Z. Shang, L. Meng, C. Zhang, M. Xiao, C. Yang, Y. Li, High efficiency polymer solar cells with efficient hole transfer at zero highest occupied molecular orbital offset between methylated polymer donor and brominated acceptor, J Am Chem Soc 142 (2020) 1465–1474.
- [32] J. Yuan, Y. Zhang, L. Zhou, C. Zhang, T.K. Lau, G. Zhang, X. Lu, H.L. Yip, S.K. So, S. Beaupre, M. Mainville, P.A. Johnson, M. Leclerc, H. Chen, H. Peng, Y. Li, Y. Zou, Fused benzothiadiazole: a building block for n-type organic acceptor to achieve high-performance organic solar cells, Adv Mater 31 (2019), e1807577.
- [33] L. Zhan, S. Li, T.-K. Lau, Y. Cui, X. Lu, M. Shi, C.-Z. Li, H. Li, J. Hou, H. Chen, Over 17% efficiency ternary organic solar cells enabled by two non-fullerene acceptors working in an alloy-like model, Energy & Environmental Science 13 (2020) 635–645.
- [34] Y. Cui, Y. Xu, H. Yao, P. Bi, L. Hong, J. Zhang, Y. Zu, T. Zhang, J. Qin, J. Ren, Z. Chen, C. He, X. Hao, Z. Wei, J. Hou, Single-junction organic photovoltaic cell with 19% efficiency, Adv Mater 33 (2021), e2102420.
- [35] J. Wang, Z. Zheng, Y. Zu, Y. Wang, X. Liu, S. Zhang, M. Zhang, J. Hou, A tandem organic photovoltaic cell with 19.6% efficiency enabled by light distribution control, Adv Mater 33 (2021), e2102787.
- [36] Z. Zheng, J. Wang, P. Bi, J. Ren, Y. Wang, Y. Yang, X. Liu, S. Zhang, J. Hou, Tandem organic solar cell with 20.2% efficiency, Joule 6 (2022) 171–184.
- [37] X. Li, S. Luo, H. Sun, H.H.-Y. Sung, H. Yu, T. Liu, Y. Xiao, F. Bai, M. Pan, X. Lu, I. D. Williams, X. Guo, Y. Li, H. Yan, Medium band-gap non-fullerene acceptors based on a benzothiophene donor moiety enabling high-performance indoor organic photovoltaics, Energy & Environmental Science 14 (2021) 4555–4563.
- [38] Z. Zhang, Y. Li, G. Cai, Y. Zhang, X. Lu, Y. Lin, Selenium heterocyclic electron acceptor with small Urbach energy for as-cast high-performance organic solar cells, J Am Chem Soc 142 (2020) 18741–18745.
- [39] F. Qi, K. Jiang, F. Lin, Z. Wu, H. Zhang, W. Gao, Y. Li, Z. Cai, H.Y. Woo, Z. Zhu, A.K. Y. Jen, Over 17% efficiency binary organic solar cells with photoresponses reaching 1000 nm enabled by selenophene-fused nonfullerene acceptors, ACS Energy Letters 6 (2020) 9–15.
- [40] C. Yang, Q. An, H.R. Bai, H.F. Zhi, H.S. Ryu, A. Mahmood, X. Zhao, S. Zhang, H. Y. Woo, J.L. Wang, A synergistic strategy of manipulating the number of selenophene units and dissymmetric central core of small molecular acceptors

enables polymer solar cells with 17.5 % efficiency, Angew Chem Int Ed Engl 60 (2021) 19241–19252.

- [41] H. Yu, Z. Qi, J. Zhang, Z. Wang, R. Sun, Y. Chang, H. Sun, W. Zhou, J. Min, H. Ade, H. Yan, Tailoring non-fullerene acceptors using selenium-incorporated heterocycles for organic solar cells with over 16% efficiency, Journal of Materials Chemistry A 8 (2020) 23756–23765.
- [42] N. Qiu, H. Zhang, X. Wan, C. Li, X. Ke, H. Feng, B. Kan, H. Zhang, Q. Zhang, Y. Lu, Y. Chen, A new nonfullerene electron acceptor with a ladder type backbone for high-performance organic solar cells, Adv Mater 29 (2017) 1604964–1604968.
- [43] X. Ke, L. Meng, X. Wan, M. Li, Y. Sun, Z. Guo, S. Wu, H. Zhang, C. Li, Y. Chen, The rational and effective design of nonfullerene acceptors guided by a semi-empirical model for an organic solar cell with an efficiency over 15, Journal of Materials Chemistry A 8 (2020) 9726–9732.
- [44] Y. Wang, Y. Zhang, N. Qiu, H. Feng, H. Gao, B. Kan, Y. Ma, C. Li, X. Wan, Y. Chen, A halogenation strategy for over 12% efficiency nonfullerene organic solar cells, Advanced Energy Materials 8 (2018) 1702870–1702876.
- [45] H. Feng, N. Qiu, X. Wang, Y. Wang, B. Kan, X. Wan, M. Zhang, A. Xia, C. Li, F. Liu, H. Zhang, Y. Chen, An A-D-A type small-molecule electron acceptor with endextended conjugation for high performance organic solar cells, Chemistry of Materials 29 (2017) 7908–7917.
- [46] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.L. Yip, Y. Cao, Y. Chen, Organic and solution-processed tandem solar cells with 17.3% efficiency, Science 361 (2018) 1094–1098.
- [47] Y. Zhang, H. Feng, L. Meng, Y. Wang, M. Chang, S. Li, Z. Guo, C. Li, N. Zheng, Z. Xie, X. Wan, Y. Chen, High performance thick-film nonfullerene organic solar cells with efficiency over 10% and active layer thickness of 600 nm, Advanced Energy Materials 9 (2019) 1902688–1902694.
- [48] X. Fan, J. Gao, W. Wang, S. Xiao, C. Zhan, X. Lu, Q. Zhang, Ladder-type nonacyclic arene bis(thieno[3,2-b]thieno)cyclopentafluorene as a promising building block for non-fullerene acceptors, Chem Asian J 14 (2019) 1814–1822.
- [49] G. Liu, R. Xia, Q. Huang, K. Zhang, Z. Hu, T. Jia, X. Liu, H.L. Yip, F. Huang, Tandem organic solar cells with 18.7% efficiency enabled by suppressing the charge recombination in front sub-cell, Advanced Functional Materials 31 (2021), 2103283.
- [50] Y. Zhang, H. Feng, L. Meng, Y. Wang, M. Chang, S. Li, Z. Guo, C. Li, N. Zheng, Z. Xie, X. Wan, Y. Chen, High performance thick-film nonfullerene organic solar cells with efficiency over 10% and active layer thickness of 600 nm, Advanced Energy Materials 9 (2019), 1902688.
- [51] M. Zhang, X. Guo, W. Ma, H. Ade, J. Hou, A large-bandgap conjugated polymer for versatile photovoltaic applications with high performance, Adv Mater 27 (2015) 4655–4660.
- [52] Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang, L. Ding, 18% Efficiency organic solar cells, Science Bulletin 65 (2020) 272–275.
- [53] Y. Jiang, K. Jin, X. Chen, Z. Xiao, X. Zhang, L. Ding, Post-sulphuration enhances the performance of a lactone polymer donor, Journal of Semiconductors 42 (2021), 070501.
- [54] K. Jin, Z. Xiao, L. Ding, D18, an eximious solar polymer, Journal of Semiconductors 42 (2021) 10502.
- [55] X. Meng, K. Jin, Z. Xiao, L. Ding, Side chain engineering on D18 polymers yields 18.74% power conversion efficiency, Journal of Semiconductors 42 (2021), 100501.
- [56] C.Y. Chang, Y.J. Cheng, S.H. Hung, J.S. Wu, W.S. Kao, C.H. Lee, C.S. Hsu, Combination of molecular, morphological, and interfacial engineering to achieve highly efficient and stable plastic solar cells, Adv Mater 24 (2012) 549–553.
- [57] R. Steyrleuthner, M. Schubert, I. Howard, B. Klaumunzer, K. Schilling, Z. Chen, P. Saalfrank, F. Laquai, A. Facchetti, D. Neher, Aggregation in a high-mobility ntype low-bandgap copolymer with implications on semicrystalline morphology, J Am Chem Soc 134 (2012) 18303–18317.
- [58] C. Li, X. Zhang, N. Yu, X. Gu, L. Qin, Y. Wei, X. Liu, J. Zhang, Z. Wei, Z. Tang, Q. Shi, H. Huang, Simple nonfused-ring electron acceptors with noncovalently conformational locks for low-cost and high-performance organic solar cells enabled by end-group engineering, Advanced Functional Materials (2021), 2108861.
- [59] A.K. Kyaw, D.H. Wang, V. Gupta, W.L. Leong, L. Ke, G.C. Bazan, A.J. Heeger, Intensity dependence of current-voltage characteristics and recombination in highefficiency solution-processed small-molecule solar cells, ACS Nano 7 (2013) 4569–4577.
- [60] M. Liu, Y. Jiang, D. Liu, J. Wang, Z. Ren, T.P. Russell, Y. Liu, Imidazolefunctionalized imide interlayers for high performance organic solar cells, ACS Energy Letters 6 (2021) 3228–3235.
- [61] S. Ma, Q. Huang, Y. Liang, H. Tang, Y. Chen, J. Zhang, K. Zhang, F. Huang, Y. Cao, Non-fullerene electron acceptors with benzotrithiophene with *π*-extension terminal groups for the development of high-efficiency organic solar cells, Journal of Materials Chemistry C 9 (2021) 13896–13903.
- [62] X.-j. Zhou, T.-t. Dai, X. Li, Y.-j. Yan, W. Xiong, T. Lin, J. Zhou, D.-h. Xu, Y.-h. Zhu, J. Zhao, A.-c. Geng, Improved charge transport and reduced carrier recombination of nonfullerene organic solar cells with the binary solvent, ACS Applied Energy Materials 4 (2021) 8175–8182.
- [63] X. Zhang, G. Li, S. Mukherjee, W. Huang, D. Zheng, L.W. Feng, Y. Chen, J. Wu, V. K. Sangwan, M.C. Hersam, D.M. DeLongchamp, J. Yu, A. Facchetti, T.J. Marks, Systematically controlling acceptor fluorination optimizes hierarchical morphology, vertical phase separation, and efficiency in non-fullerene organic solar cells, Advanced Energy Materials (2021), 2102172.
- [64] T. Wang, M.K. Ravva, J.-L. Brédas, Impact of the nature of the side-chains on the polymer-fullerene packing in the mixed regions of bulk heterojunction solar cells, Advanced Functional Materials 26 (2016) 5913–5921.

M. Li et al.

- [65] W. Li, M. Chen, J. Cai, E.L.K. Spooner, H. Zhang, R.S. Gurney, D. Liu, Z. Xiao, D. G. Lidzey, L. Ding, T. Wang, Molecular order control of non-fullerene acceptors for high-efficiency polymer solar cells, Joule 3 (2019) 819–833.
- [66] Z. Wang, Z. Peng, Z. Xiao, D. Seyitliyev, K. Gundogdu, L. Ding, H. Ade, Thermodynamic properties and molecular packing explain performance and processing procedures of three D18:NFA organic solar cells, Adv Mater 32 (2020), e2005386.
- [67] U. Rau, B. Blank, T.C.M. Müller, T. Kirchartz, Efficiency potential of photovoltaic materials and devices unveiled by detailed-balance analysis, Physical Review Applied 7 (2017) 44016.
- [68] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T.P. Russell, Y. Cao, Singlejunction polymer solar cells with high efficiency and photovoltage, Nature Photonics 9 (2015) 174–179.
- [69] M. Kuik, L.J. Koster, G.A. Wetzelaer, P.W. Blom, Trap-assisted recombination in disordered organic semiconductors, Phys Rev Lett 107 (2011), 256805.

- [70] T. Kirchartz, J. Nelson, Meaning of reaction orders in polymer:fullerene solar cells, Physical Review B 86 (2012), 165201.
- [71] T. Kirchartz, B.E. Pieters, J. Kirkpatrick, U. Rau, J. Nelson, Recombination via tail states in polythiophene:fullerene solar cells, Physical Review B 83 (2011), 115209.
- [72] J. Yao, T. Kirchartz, M.S. Vezie, M.A. Faist, W. Gong, Z. He, H. Wu, J. Troughton, T. Watson, D. Bryant, J. Nelson, Quantifying losses in open-circuit voltage in solution-processable solar cells, Physical Review Applied 4 (2015) 14020.
- [73] F. Urbach, The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids, Physical Review 92 (1953), 1324-1324.
- [74] S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He, H. Wu, Y. Cao, High-efficiency organic solar cells with low non-radiative recombination loss and low energetic disorder, Nature Photonics 14 (2020) 300–305.
- [75] P. Bi, S. Zhang, Z. Chen, Y. Xu, Y. Cui, T. Zhang, J. Ren, J. Qin, L. Hong, X. Hao, J. Hou, Reduced non-radiative charge recombination enables organic photovoltaic cell approaching 19% efficiency, Joule 5 (2021) 2408–2419.